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Spatial variations in the levels and isomeric patterns of PBDEs and HBCDs in the European eel in Flanders

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ABSTRACT

Pooled yellow eel (*Anguilla anguilla* L.) samples, consisting of 3–10 eels, from 50 locations collected in the period 2000–2006 were used to assess the pollution with PBDEs and HBCDs in Flemish waters (Belgium). Results from this monitoring network are presented and the spatial aspect throughout Flanders is included, linking POP levels to the industrial characteristics of the different sampling locations. The following PBDE congeners were measured using GC/MS: 28, 47, 49, 66, 85, 99, 100, 153, 154, 183 and 209. Concentrations of ∑PBDE ranged between 10 and 5811 ng/g lipid weight (lw) with a median value of 81 ng/g lw. BDE 47 dominated the PBDE profile in the majority of the eel samples, except for six samples, in which BDE 209 was the dominating congener. These latter samples are probably associated with recent exposure to the Deca-BDE mixture. Three HBCD diastereoisomers (α-, β- and γ-HBCD) were measured using LC/MS-MS. ∑HBCDs ranged between 16 and 4397 ng/g lw, with a median value of 73 ng/g lw. α-HBCD was the dominant isomer in all eel samples. Sediment concentrations of PBDEs were available from four locations and were used to compare the PBDE profile with those in eel. An important shift in the profile was observed, especially for BDE 209. While BDE 209 was only found in 12 eel samples, it was the dominant congener in all sediment samples. This could be due to its metabolisation or degradation in biota combined with the poor uptake of BDE 209 from sediments and its very low water solubility. No HBCDs were detected in any of the sediment samples. No significant correlation could be found between concentrations of PBDEs in eel and sediment from the same location. Comparison with previous studies shows that PBDE and HBCD levels in Flemish eels have decreased rapidly between 2000 and 2006 at particular sites, but alarming concentrations can still be found at industrialized hot spots. This finding is reflected in the human exposure to PBDEs and HBCDs through eel consumption. For average consumers (2.9 geel/day), intakes ranged between 3 and 2295 ng/day for ∑PBDEs (with a median value of 16 ng/day) and between 3 and 1110 ng/day for ∑HBCDs (with a median value of 18 ng/day), respectively. Additionally, human intakes were calculated for recreational fishermen, eating up to 12 g or 86 geel/day. Intakes of those risk groups were higher in comparison with average consumers and were above reference doses described in literature which may induce adverse effects.

1. Introduction

Brominated flame retardants (BFRs) have been extensively used in consumer products such as plastics, textiles, furnishing foam, and electronic circuit boards (Rahman et al., 2001) to reduce the risk of fire and meet fire safety regulations (Alaee et al., 2003). Once released from these consumer products (during production, recycling procedures or usage) BFRs tend to be stable and persist in both terrestrial and aquatic environments. Additive BFRs, such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs), are more easily released into the environment compared to their reactive counterparts because they are not chemically bound to the matrix. Due to their toxic effects, including endocrine disruption at the level of the thyroid gland and reproduction system, the usage of Penta- and Octa-BDE mixtures has been banned in Europe since August 2004 (Directory 2003/11/EC). Evidence of environmental debromination of BDE 209 leads to its restricted use in July 2008 by the European court of justice (Betts, 2008). HBCD usage is currently still allowed although risk analysis showed HBCD fulfils all Persistent, Bio-accumulative and Toxic (PBT) criteria and is included in the PBT list of the European chemical substance information system (ESIS). Despite these efforts, high environmental levels have recently been found near sites of human activity (Roosens et al., 2008) which demonstrates the importance of ongoing monitoring studies.

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The aims of the present study were to investigate current PBDE and HBCD distribution in eels throughout a bio-monitoring network in the freshwater system in Flanders and to compare the isomeric profiles of PBDEs and HBCDs in eels and sediments from the most polluted areas. As fish is an important part of human diet, human exposure through intake of Flemish eel was assessed for both the normal Flemish population and for risk groups such as recreational fishermen. European eel (*Anguilla anguilla* L.) in its yellow eel stage was chosen as bio-indicator for the monitoring of environmental contaminants as this stage is characterised by primarily sedentary behaviour (Belpaire and Goemans, 2007). Eel analysis gives a representative description of contamination patterns surrounding the area where it was caught. Furthermore, eel is a fatty fish species, assuring an optimal accumulation of lipophilic contaminants, such as BFRs (Belpaire, 2008). The current study expands the knowledge regarding PBDE and HBCD concentrations, their patterns, distribution profiles and time trends in the freshwater system in Flanders.

2. Materials and methods

2.1. Samples

Yellow eels were collected between 2000 and 2006, from 50 various locations throughout Flanders (Belgium) by the Flemish Research Institute for Nature and Forest (INBO) (Fig. 1). Locations are situated in the catchments of the rivers Ijzer, Scheldt and Meuse and were characterised as rivers or brooks, canals, polder water courses or closed water bodies such as old meanders, ponds or lakes (Table 1). Fish were collected using fyke nets or electro-fishing techniques. Between 3 and 10 eels were caught per location, an amount ranging between 1 and 4 g of their muscle tissue was pooled and analysed for PBDE congeners (28, 47, 49, 66, 99, 100, 154, 153, 183 and 209) and HBCD (α-, β- and γ-) isomers. Detailed information on the number of eels per pooled sample, the size range, weight range, lipid range and sex are given in Table 1.

2.2. Analytical methods

PBDEs reference standards were bought from Wellington Laboratories (Guelph, ON, Canada) and Accustandard (New Haven, CT, USA). Standards of individual ^{12}C-HBCD and ^{13}C-HBCD isomers were purchased from Wellington Laboratories. All solvents used for the analysis (acetone, dichloromethane, *iso*-octane, *n*-hexane, and methanol) were of SupraSolv® grade (Merck, Darmstadt, Germany). Sodium sulphate (Merck) and silica gel (0.063–0.200 mm, Merck) were prewashed with *n*-hexane and heated overnight at 150 °C before use. Extraction thimbles (25 × 100 mm, Whatman®, England) were pre-extracted for 1 h with hexane/acetone (3/1; *v*/*v*) and dried at 100 °C for 1 h. Empty polypropylene columns for clean-up (25 mL) were purchased from Alltech (Lokeren, Belgium).

About 1 g pooled eel muscle sample was weighed, homogenised with Na_2SO_4 and spiked with internal standards (BDE 77, BDE 128, ^{13}C-BDE 209, ^{13}C-α-HBCD,^{13}C-β-HBCD and ^{13}C-γ-HBCD), hot Soxhlet extracted during 2 h with hexane:acetone (3:1) and cleaned-up on acidified silica (Voorspoels et al., 2003). Prior to the clean-up, a fraction of the extract was taken to determine the lipid content gravimetrically. Minor adaptations were required as PBDEs were analysed with GC–ECNI/MS and HBCDs with LC–MS/MS. The cleaned extract was evaporated to dryness, redissolved in 0.5 mL hexane and eluted from pre-packed silica cartridges (Varian) with 6 mL hexane (for GC analysis) and 6 mL DCM (for LC analysis). Both fractions were evaporated to incipient dryness and redissolved in 100 μL *iso*-octane and 100 μL methanol, respectively.

The determination of PBDEs was performed with an Agilent 6890GC-5973MS equipped with a 15 m × 0.25 mm × 0.10 μm DB-5 capillary column and operated in electron capture negative ionisation (ECNI) mode. The ion source, quadrupole and interface temperatures were 250, 150 and 300 °C, respectively. Helium was used as carrier gas at constant flow (1.0 mL/min) and with methane as moderating gas. The MS was operated in SIM mode (*m*/*z* 79 and 81 were monitored for the entire run, *m*/*z* 487 and 495 were monitored for BDE 209 and ^{13}C-BDE 209, respectively). Dwell times were set to 40 ms. One μl of

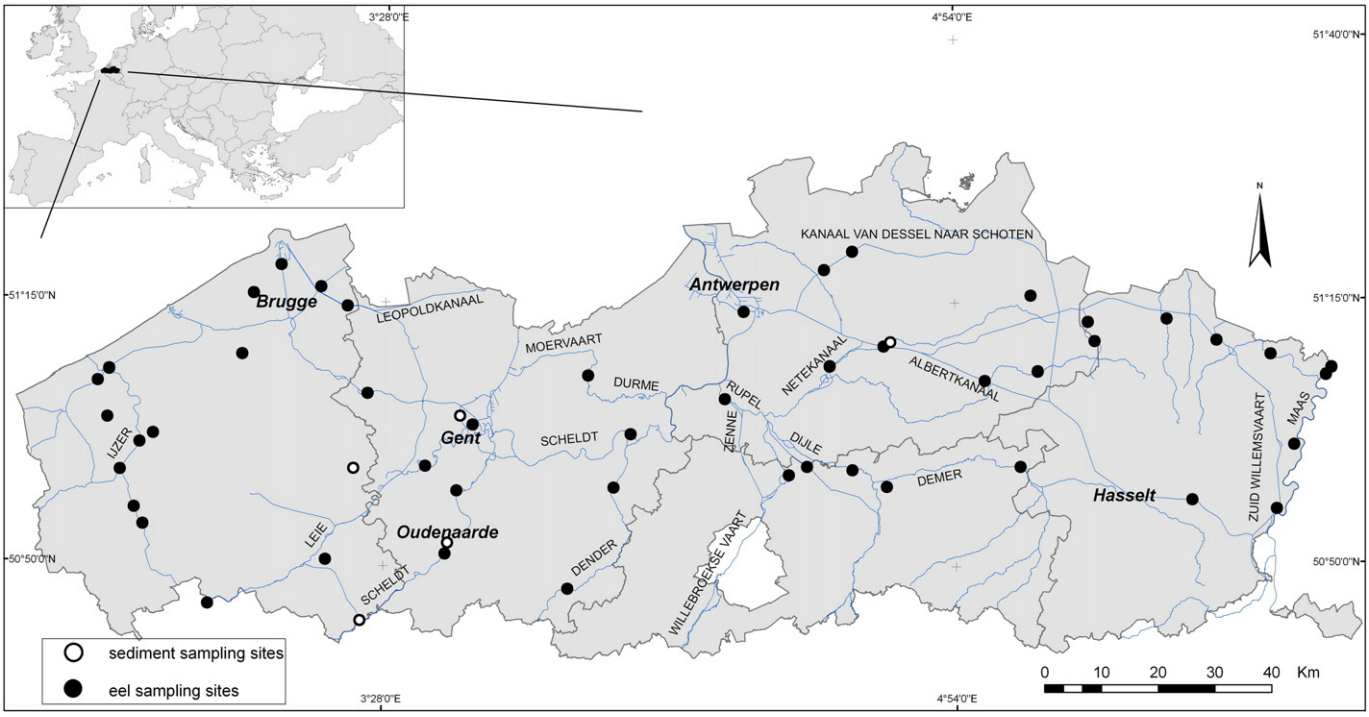

Fig. 1. Locations used for eel and sediment samplings.

the extract was injected in solvent vent mode and the splitless time was 1.50 min. The oven temperature was programmed from 90 °C, kept for 1.5 min, then increased with 15 °C/min to 295 °C, kept for 15 min.

The determination of ΣHBCDs and separation of α-, β-, and γ-HBCD was achieved using a dual pump Agilent 1100 Series liquid chromatograph equipped with autosampler and vacuum degasser. An Agilent Zorbax Extended-C18 reversed phase analytical column (50 mm × 2.1 mm i.d., 3.5 μm particle size) was used. A mobile phase of (a) water and (b) methanol at a flow rate of 200 μL/min was applied for elution of HBCD isomers; starting at 75% (b) then increased linearly to 100% (b) over 7 min; this was held for 12 min followed by a linear decrease to 75% (b) over 0.5 min and held for 10 min. The target analytes were baseline separated on the LC column with retention times of 7.0, 7.5, 7.8 min for α-, β- and γ-HBCD respectively. Mass spectrometric analysis was performed using an Agilent 6410 triple quadrupole mass spectrometer operated in the ES negative ion mode. MS/MS detection operated in the MRM (multiple reaction monitoring) mode was used for quantitative determination of the HBCD isomers based on *m/z* 640.6 to 79 and *m/z* 652.6 to 79 for the native and ^{13}C-labelled diastereomers, respectively.

The analytical procedures were validated through analysis of procedural blanks, duplicate samples, and certified material SRM 1945 (PBDEs in whale blubber, which has also indicative values for HBCDs). Obtained values were not deviating with more than 10% from the certified values and all samples were blank-corrected. Recoveries of internal standards were all above 80% (Table SI-1). Method quantification limits (LOQs) for individual PBDE congeners and individual HBCD diastereomers were based on procedural blanks (10 × SD) and the amount of sample taken for analysis (typically 1 g eel muscle). LOQs for tri-hepta PBDEs range between 1 and 2 ng/g lipid weight (lw), for BDE 209 LOQ was 10 ng/g lw, while LOQs were 1, 2 and 2 ng/g lw for α-, β- and γ-HBCD, respectively. Samples with concentrations below LOQ were calculated as $f \times$ LOQ with f being the fraction of samples above LOQ.

3. Results and discussion

3.1. Levels

In total, 50 pooled eel muscle tissue samples were analysed and lipid percentage varied between 2.0 and 20.8%. ΣPBDEs ranged between 10 and 5811 ng/g lw with a median value of 81 ng/g lw (Table 2, Fig. 2). The majority of the samples (46 out of 50 samples) were characterised by tri-hepta BDE levels <200 ng/g lw, whereas three eel samples contained PBDE levels up to 1200 ng/g lw. One even higher contaminated sample, containing 5811 ng/g lw, was found. A similar broad contamination profile was seen for ΣHBCDs, ranging between 14 and 4397 ng/g lw with a median value of 73 ng/g lw (Table 2, Fig. 2). The majority (34 out of 50) of samples contained ΣHBCD levels <200 ng/g lw, while 11 samples contained levels between 400 and 900 ng/g lw and five samples contained levels in excess of 1000 ng/g lw. A large concentration range is covered for both compounds throughout Flanders, in this sampling grid used in the last 15 years for the monitoring of PCBs and pesticides (Maes et al., 2008). Median percentage lipid content per pooled sample (Table 1) could not be correlated with the corresponding ΣPBDE and ΣHBCD levels (Fig. SI-1).

3.2. Comparison with other studies

Comparison between studies is liable to large variations as BFR concentrations largely depend on the sampling location and on the year of sampling, as levels tend to stabilize or decline due to regulatory measures (Fangström et al., 2008, Law et al., 2008). The important influence of geographical and annual characteristics of a study on POP contamination is supported as the majority of current eel samples contain similar Σtri-hepta BDE levels compared to other recent European studies and after removal of the most contaminated samples ($n = 4$, range 200–5811 ng/g lw) (Table 2). ΣHBCDs cover an equally broad range compared to what has been seen recently in the Netherlands (Van Leeuwen and De Boer, 2008), although the median value in the latter study is an order of magnitude higher, indicating the presence of more highly contaminated sampling sites in the Netherlands than Belgium. Maximal PBDE and HBCD eel concentrations, collected in 2000 in the area of Oudenaarde (Belpaire et al., 2003) were a factor 6 higher compared to the levels reported in the present study in eels collected in 2006, which suggests a descending trend between 2000 and 2006.

3.3. Geographical variation

The broad range in PBDE and HBCD concentrations monitored in the current study is likely due to the large variety in sampling locations, from highly industrialized areas to small rural creeks (Fig. 2). For both PBDEs and HBCDs, some of the most contaminated eel samples were caught in the river Scheldt, near a highly industrialized area called Oudenaarde. This region is part of a bio-monitoring network for environmental contaminants such as PCBs and PBDEs. The purpose for sampling the tideway of the river Scheldt was the previously reported high HBCD levels in biota and sediment samples from this region (de Boer et al., 2001) and the presence of intensive textile industry downstream and upstream from Antwerp (Fig. 2). The textile industry is important in Flanders as it represents 85% of the total Belgian textile production, mostly tapestry and cotton. Eel collected from this region in 2000 (a pool of 3 female eels, length 38–57 cm; weight 100-405 g) contained a maximum ΣPBDEs (BDE 28, 47, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 183, 190 and 209) of 31,640 ng/g lw and ΣHBCDs of 33,000 ng/g lw (Belpaire and Goemans, 2002). Although eel collected in 2006 (Table 1, sample 45) was still contaminated compared to other regions in Flanders, median levels in eel decreased to 1200 ng/g lw ΣPBDEs and 1500 ng/g lw ΣHBCDs. These data indicate a significant decline in both PBDE and HBCD levels, which might be associated with regulatory measures taken for both BFRs, and have been reflected in other biota too (Law et al., 2008). The highest PBDE (5811 ng/g lw) and high HBCD (3530 ng/g lw) levels in the current study were found in a location ~14 km downstream of Oudenaarde, also located on the river Scheldt, but closer to its mouth (Fig. 2). Overall, HBCD distribution patterns showed a more widespread usage compared to PBDEs in the surrounding region of Oudenaarde. As reported in previous studies, both PBDE and HBCD contaminations seem to be largely related to the presence of human activities (Allchin and Morris, 2003) which stress the need for ongoing monitoring of POPs (Table 3).

3.4. Profiles in eel

BDE 47 was the dominant congener in most eel samples ($n = 44$) and accounted on average 60 ± 18% of Σtri-hepta PBDEs, followed by BDE 100 (19%) and BDE 99 (5%) (Fig. 3). Ashley et al. (2007) reported similar PBDE profiles in American eel (*A. rostrata*) samples and suggested high BDE 47 and low BDE 99 levels were a possible outcome of metabolic pathways, present in eels. Such pathways have been described for carp (*Cyprinus carpio carpio* L.) by Stapleton et al. (2006). Thus, BDE 47/BDE 99 ratios give an estimate of the time of exposure as high ratios are indicative of past exposure and low ratios indicate recent exposure. Calculating BDE 47/BDE 99 levels for our eel samples, a large variety in ratios can be distinguished (Fig. 4), which suggest both past and recent exposures of Flemish eels. Due to the ban or restricted use of all PBDE congeners in the EU, recent exposure occurs most likely due to the release of PBDEs which have accumulated in matrices, such as soils and sediments. Eel, primarily a benthic feeder, is more prone to accumulate pollutants also from sediments. Thus the

Table 1
Description of sampling sites, number and parameters of eels (length, weight and lipid percentage) constituting the pools, together with total concentrations of PBDEs and HBCDs (in ng/g lipid weight). All eels investigated in the present study are yellow eels.

Pool	Location	Water course	Morphotype	Water course type	Municipality	*N*	Gender	Length (cm)	Weight (g)	Lipid (%)	ΣPBDEs (ng/g lw)	ΣHBCDs (ng/g lw)
1	Urlobroek	Abeek	Creek	River	Maaseik	6	Female (3) Undetermined (3)	33–58	59–293	3.6	46	71
2	Langerlo, sluis	Albertkanaal	Canal	Canal	Genk	7	Female (5) Undetermined (2)	36–45	71–160	8.9	94	59
3	Zuienkerke, Zielebrug	Blankenbergse vaart	Polder water course	Polder	Houthave	10	Undetermined (10)	35–39	86–118	12.7	4	28
4	Gent	Oude Leie Bourgoyen	Creek	Old meander	Gent	10	Female (3) Undetermined (7)	37–43	63–120	8.7	149	495
5	Lissewege	Bouwdewijnkanaal	Polder water course	Canal	Heist	4	Female (4)	58–76	354–1036	4.9	25	525
6	Oostkerkebrug	Damse vaart	Polder water course	Canal	Westkapelle	9	Female (3) Undetermined (6)	37–48	86–162	5.7	29	108
7	Idegem, sluis	Dender	Creek	River	Geraardsbergen	7	Female (5) Undetermined (2)	45–57	139–292	6.2	108	59
8	Hofstade	Dender	Creek	River	Aalst	9	Female (4) Undetermined (5)	39–52	88–256	7.2	137	72
9	Appels, Dendermonde	Dender	Creek	River	Dendermonde	8	Female (4) Undetermined (4)	35–48	96–207	15.4	556	205
10	Diest	Demer	Creek	River	Diest	3	Female (2) Undetermined (1)	35–61	63–520	17.6	113	56
11	Harelbeke	Gavers	Closed water	/	Harelbeke	5	Female (5)	51–65	181–542	21.4	22	41
12	grens Haacht-Keerbergen, Hansbrug	Dijle	Creek	River	Haacht	3	Female (3)	42–63	116–538	4.9	126	124
13	Overpelt	Dommel	Creek	River	Overpelt	9	Female (3) Undetermined (6)	30–52	46–223	7.0	45	99
14	Meerhout, Hulsen	Grote Nete	Creek	River	Meerhout	7	Female (2) Undetermined (5)	36–44	61–152	10.2	44	26
15	Diksmuide	Handzame vaart	Polder water course	Polder	Diksmuide	10	Undetermined (10)	32–37	44–73	11.5	76	113
16	Boezinge, SA Boezingebrug	Ieperkanaal	Polder water course	Canal	Ieper	10	Female (2) Undetermined (8)	34–44	61–145	11.8	29	70
17	Mol	Kanaal van Beverlo	Canal	Canal	Lommel	10	Female (5) Undetermined (5)	43–49	130–353	5.6	57	35
18	Lommel	Kanaal van Beverlo	Canal	Canal	Lommel	10	Female (5) Undetermined (5)	36–45	72–153	6.0	89	69
19	Brecht, Eindhoven	Kanaal van Dessel naar Schoten	Canal	Canal	Brecht	10	Female (5) Undetermined (5)	34–48	53–214	2.4	67	109
20	Sint-Job -in't-Goor	Kanaal van Dessel naar Schoten	Canal	Canal	Brecht	10	Female (8) Undetermined (2)	39–56	76–311	19.0	87	58
21	Hollebeek - Aalter	Kanaal Gent-Oostende	Polder watercourse	Canal	Knesselare	6	Female (3) Undetermined (6)	33–48	54–217	7.7	170	4287
22	SA Sifon Albert-kanaal - Bouwel	Kleine Nete	Creek	River	Berlaar	10	Female (3) Undetermined (7)	34–49	58–216	9.6	123	79
23	grens Koksijde -Nieuwpoort	Kanaal van Nieuwpoort	Canal	Canal	Nieuwpoort	10	Female (2) Undetermined (8)	35–45	79–185	10.9	22	78
24	Wervik	Leie	Creek	River	Wervik	6	Female (6)	41–77	133–997	12.3	238	219
25	Moerkerke, Damme kmp 15	Leopold Kanaal	Polder watercourse	Canal	Moerkerke	9	Female (1) Undetermined (8)	31–43	45–117	12.7	14	34

26	Kinrooi	Grensmaas	Creek	River	Ophoven	10	Female (10)	41–49	109–213	20.8	101	67
27	Stokkem	Oude Maas	Closed water		Stokkem	10	Female (6) Undetermined (4)	37–44	71–148	2.0	37	72
28	Rotselare	Rotselare meer	Closed water		Rotselaar	10	Female (3) Undetermined (7)	37–41	88–111	5.8	121	31
29	Niel, oude arm, sluis Wintam	Willebroekse vaart	Canal	Canal	Hoboken	10	Female (1) Undetermined (9)	32–42	42–132	10.6	110	82
30	Diksmuide, Heernisse	Ijzer	Polder watercourse	River	Diksmuide	5	Female (3) Undetermined (2)	31–61	56–511	16.4	66	877
31	Geel, Stelen	Albertkanaal	Canal	Canal	Geel	7	Female (3) Undetermined (4)	38–53	93–197	9.4	30	57
32	Overpelt	Dommel	Creek	River	Overpelt	10	Female (7) Undetermined (3)	31–51	56–216	9.2	60	156
33	Zuidschote-Bikschote, steenstratebrug	Ieperkanaal	Polder watercourse	Canal	Ieper	10	Female (2) Undetermined (8)	32–41	72–123	10.5	18	18
34	Houthulst, monding Yzer	Ieperkanaal	Polder watercourse	Canal	Lo-Reninge	10	Female (1) Undetermined (9)	34–40	90–135	17.7	21	16
35	Snellegem-Jabbeke	Jabeekse beek	Creek	River	Zedelgem	10	Female (3) Undetermined (7)	31–49	50–269	10.2	81	29
36	Lommel	Kanaal van Beverlo	Canal	Canal	Lommel	10	Female (6) Undetermined (4)	35–88	67–1039	9.4	24	32
37	Boortmeerbeek, stroomopwaarts sas	Kanaal van Leuven naar de Dijle	Canal	Canal	Zemst	10	Female (7) Undetermined (3)	38–50	81–225	6.7	15	20
38	Deinze, Leiehoek	Leie	Creek	River	Deinze	9	Female (3) Undetermined (6)	35–46	69–180	6.9	293	4397
39	Stevensweert, Molensteen	Grensmaas	Creek	River	Ophoven	9	Female (6) Undetermined (3)	36–49	76–209	6.3	87	123
40	Daknam	Moervaart	Creek	Polder	Lokeren	10	Female (7) Undetermined (3)	34–48	80–221	6.6	805	1160
41	Lier, Het Alliers	Netekanaal	Canal	Canal	Lier	10	Female (2) Undetermined (8)	35–45	46–116	11.8	30	97
42	Lier, Het Alliers	Netekanaal	Canal	Canal	Lier	9	Female (2) Undetermined (7)	35–45	67–145	14.0	23	78
43	Nieuwpoort	Kanaal Nieuwpoort-Plassendale	Canal	Canal	Nieuwpoort	10	Female (4) Undetermined (6)	40–45	107–150	12.2	41	22
44	Pervijse (Rousdamme)	Oude A-vaart	Polder watercourse	Polder	Lampernisse	10	Female (3) Undetermined (7)	32–47	59–197	11.0	7	14
45	Oudenaarde, stroomafw.	Schelde	Creek	River	Oudenaarde	5	Female (3) Undetermined (2)	35–45	62–145	12.7	1249	1526
46	afw. Moerbeek - Eke-Gavere	Schelde	Creek	River	Gavere	10	Female (7) Undetermined (3)	35–46	68–210	13.6	5811	3530
47	St.-Anneke, kerk Oosterzeel - Antwerpen LO	Schelde	Tidal water	River	Antwerpen	10	Female (2) Undetermined (8)	35–44	72–156	7.1	267	334
48	Weerde	Meer van Weerde	Closed water		Weerde	7	Female (2) Undetermined (5)	32–42	44–121	5.1	276	74
49	Retie	Witte Nete	Creek	River	Retie	10	Female (5) Undetermined (5)	33–47	52–132	8.8	25	79
50	Rekem, jachthaven	Zuid-Willemsvaart	Canal	Canal	Maasmechelen	10	Female (4) Undetermined (6)	35–44	77–153	11.5	64	48

Table 2
PBDE and HBCD concentrations (ng/g lw) in eel from current and previous studies.

ng/g lw	ΣPBDEs			ΣHBCDs			Reference
Country	Average	Median	Range	Average	Median	Range	
Belgium[a]	242	81	10–5811	394	73	16–4397	Present study
Belgium[b]	830	–	660–1010	7900	–	2600–10,100	Roosens et al. (2008)
Belgium[c]	–	–	x–32,000	–	–	<2–33,000	(Belpaire and Goemans, 2002; Belpaire et al., 2003)
Belgium	–	–	–	43	–	<1–266	Morris et al. (2004)
France[d]	–	40	26–108	–	–	–	Bragigand et al. (2006)
Germany[e]	–	–	50–95	–	–	1753–2490	Santillo et al. (2005)
Spain[e]	–	–	18–37	–	–	624–1174	Santillo et al. (2005)
The Netherlands[f]	504	226	0.3–3287	1379	884	<0.1–5060	Van Leeuwen and De Boer (2008)
Italy[g]	–	–	0.9–14.1	–	–	–	Mariottini et al. (2008)
USA[h]	1169	862	10–5652	–	–	–	Ashley et al. (2007)

With [a]sum BDE 28, 49, 47, 66, 100, 99, 85, 154, 153, 183 and 209, with [b]sum BDE 28, 47, 49, 66, 99, 100, 153, 154 and 183, with [c]sum BDE 28, 47, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 183, 190 and 209, with [d]sum BDE 28, 47, 99, 100, 153 and 154, with [e]sum BDE 47, 99 and 100, with [f]sum BDE 28, 47, 99, 100, 154, 183 and 209, with [g]sum BDE 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 153 and 154, with [h]sum BDE 17, 25, 28 + 33, 30 47, 49, 66, 71, 75, 85 + 155, 99, 100, 116, 119, 138, 153, 154, 156, 181, 183, 190, 191, 203, 205, 206 and 209.

monitoring of sediment remains useful for further studies as indirect release of POPs in the environment is likely to become more important.

BDE 209 could only be quantified in 12 samples with concentrations ranging from 10 up to 87 ng/g lw (Fig. 3). Despite its low detection frequency, BDE 209 is the dominant congener in 6 out of the 12 samples which indicates recent and high exposure to this compound in certain locations (Fig. 3). Presence of BDE 209 in eel muscle tissue is not associated with high Σtri-hepta PBDE congeners, indicating a different source of origin. A BDE 209 hotspot seems to be present in the region surrounding Bruges. Dominance of BDE 47 combined with low BDE 209 levels, is a congener pattern seen in several studies focussing on aquatic biota (Roosens et al., 2008; Ashley et al., 2007) and is indicative of the former use of the Penta-BDE mixture (Luross et al., 2002), combined with low bioavailability of BDE 209 (Nyholm et al., 2009).

α-HBCD was the dominant isomer in all eel samples (average 85%) although the HBCD technical mixture is mainly composed of γ-HBCD. The following three factors might be responsible for this observation: 1) bio-isomerization of β- and γ-HBCD to α-HBCD as observed in fish (Law et al., 2006), 2) α-HBCD has a higher water solubility (49 μg/L) than β- and γ-HBCD (2 μg/L) and thus, is more readily available for uptake (Hunziker et al., 2004) and 3) *in vitro* experiments with rat and harbour seal microsomes showed that the biotransformation of β- and γ-HBCD was faster than that of α-HBCD (Zegers et al., 2005). Recently, photolytic degradation of γ- to α-HBCD in dust has been reported, leading to possible higher exposure to this isomer (Harrad et al., 2009) and thermal treatment induces the kinetics of this isomeric shift (Heeb et al., 2008). Therefore, industrial discharge of textile and plastic industries might contain a higher proportion of α-HBCD, as HBCD is incorporated in various products by heating (Heeb et al., 2008).

3.5. Profiles in sediment

PBDE (sum of congeners 28, 47, 66, 85, 99, 100, 153, 154, 183 and 209) results for five sediment samples were obtained by courtesy of the Flemish Environment Agency (VMM) (De Cooman, personal communication). These sediments were samples through a separate monitoring network than the eel monitoring network and sample locations could not always be matched between the two sampling networks (Fig. 1). Sediment samples were collected between 2005 and 2006 and comprised all particle fractions. Additional data can be found in Table SI-2. Sediment samples were characterised by low Σtri-hepta PBDEs concentrations between <2–65 ng/g dw, but high BDE 209 levels ranging from 20 up to 2400 ng/g dw. This shift in the PBDE congener profile compared to eel is due to different bioavailability and bioaccumulation potentials between PBDE congeners. Due to its

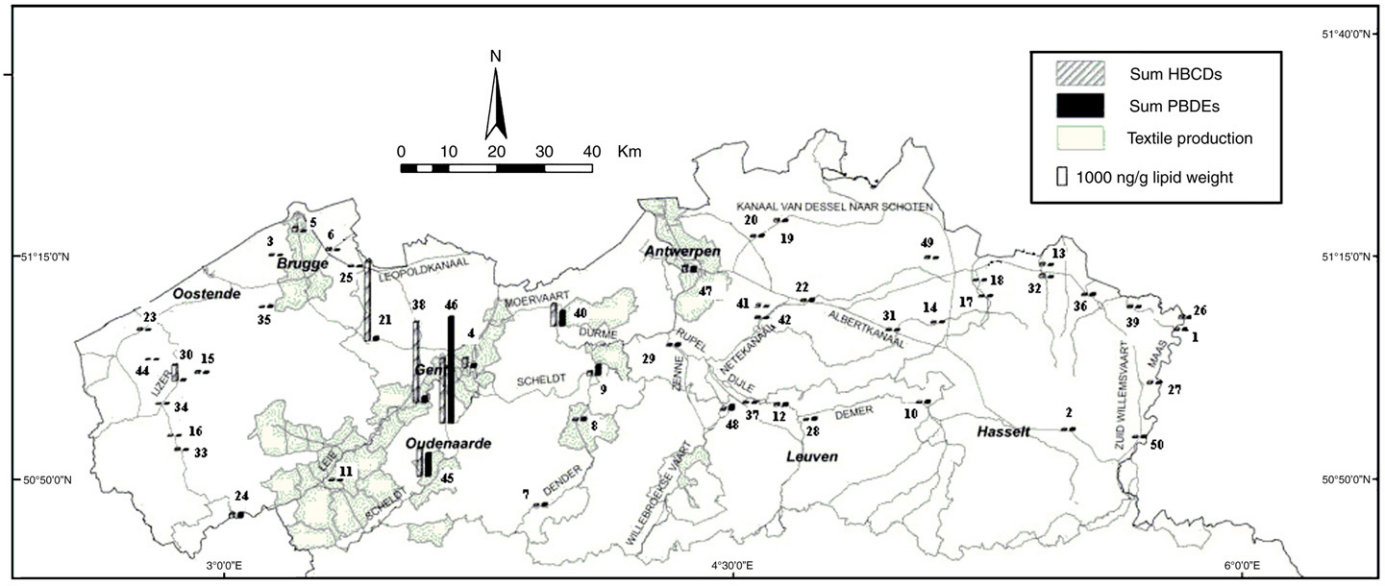

Fig. 2. Geographic distribution of PBDE and HBCD levels in eels in relation to textile industry. PBDE and HBCD profiles in eels, linked to industrialization (textile, production of electric/electronic devices and plastic industry).

Table 3
Calculated human PBDE- and HBCD-intake through eel consumption for both the average Belgian population and risk groups in ng/day with group A taking every catch home and eating all of it (86 g/day) and group B taking their catch home sometimes and eating half of it (12 g/day) (Bilau et al. 2007).

Population	Eel consumption (g/day)	∑PBDEs		∑HBCDs	
		Median	Range	Median	Range
Normal	2.9	16	3–2295	18	3–1110
Risk group A	86	472	94–68,000	534	95–32,800
Risk group B	12	66	13–9500	75	13–4600

structural formation and high molecular weight, BDE 209 is expected to be less bioavailable compared to other, smaller congeners, such as BDE 47 (Burreau et al., 2000). However, Eljarrat et al. (2007) described bioavailability of higher BFRs, such as BDE 209, in highly contaminated surroundings. BDE 209 sediment concentrations ranging up to 12 μg/g dw, led to the detection of BDE 209 in 14 out of 15 fish muscle tissue samples with concentrations up to 700 ng/g lw (Eljarrat et al., 2007). The presence of BDE 209 in Belgian sediment is probably not high enough to efficiently transfer this congener to biota. Therefore, abiotic monitoring in sediments seems to be the appropriate pathway for tracking local BDE 209 contamination, although BDE 209 levels in biota are indicative for the bioaccumulation potential.

PBDE profiles in eel and sediment samples were compared for the closest matching locations ($n=5$), but no correlation was found for PBDE congeners 47, 99, 100, 153 and 154. Concentrations of ΣHBCDs were below LOQ in all sediment samples and no correlation could be thus calculated.

3.6. Effects on the eel

The European eel is in strong decline. Recruitment has come down to only 1–5% compared to 30 years ago. The causes of the stock decline are still not elucidated, but in recent years some reports have suggested contaminants may be regarded as a potential cause (Robinet and Feunteun, 2002; Palstra et al., 2006; Belpaire et al., 2009). Both the reduction of the lipid energy as a consequence of (specific) contaminants, and the mobilization of high loads of toxic chemicals during migration, seem to be key elements decreasing probability of a successful migration and normal reproduction (Geeraerts and Belpaire, 2009). Specific effects of BFRs on the eel have not been documented until now, but considering the BFR load measured in eels, and the toxic effects demonstrated in other organisms (Hajslova et al., 2007;

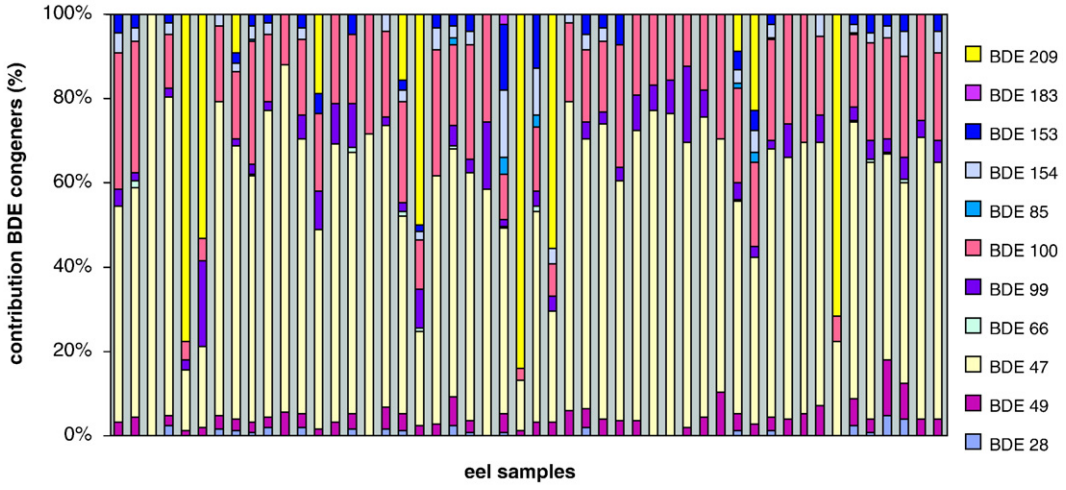

Fig. 3. Percentage profile of PBDE congeners in eel samples.

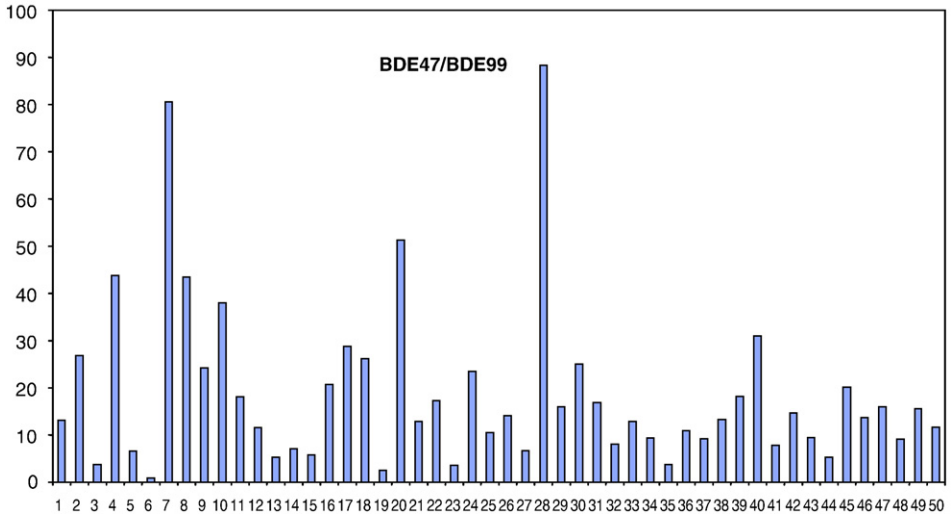

Fig. 4. Ratios between BDE 47 and BDE 99 in the eel samples.

Table 4
Oral RfD values for brominated flame retardants deducted by US-EPA-IRIS and oral RfD for HBCD from NRC (2000).

Compound	RfD (ng/kg/day)	Tested organism	Toxicological effect	Reference
BDE 47	100	Mouse	Neurological behavioural effects	Eriksson et al., 2001
BDE 99	100	Mouse	Neurological behavioural effects	Viberg et al., 2004
BDE 153	200	Mouse	Neurological behavioural effects	Viberg et al., 2003a
BDE 209	7000	Mouse	Neurological behavioural effects	Viberg et al., 2003b
HBCD	200	Rat	Weight accumulation–fat accumulation in the liver	Zeller and Kirsch, 1970

Norman et al., 2007; Rattfelt et al., 2008), it is likely to accept that BFRs put also additional pressure on the eel.

3.7. Effects on human intake of BFRs

Dietary intake is an important pathway for human exposure to BFRs (Roosens et al., 2009a,b) and fish contributes much to the total human dietary exposure (Voorspoels et al., 2007). Especially the consumption of more fatty and polluted fish species such as the eels discussed in the present study can influence dietary exposure to a large extent. As there are no professional eel fisheries in Flanders, consumption of Flemish wild eel occurs mainly by recreational fishermen and their families. Calculating daily PBDE intake through eel, based on a consumption rate of 2.9 g/day (Bilau et al., 2007), the majority of the analysed eels ($n=46/50$) are responsible for an intake <100 ng/day (Table 3). Consumption of the more contaminated eel samples led to higher exposures, ranging between 153 and 2295 ng/day. An identical trend can be observed for HBCDs with a dietary intake <100 ng/day based on 43/50 samples and a higher range between 113 and 1106 ng/day ($n=7/50$). The large variability has a more profound impact on PBDE and HBCD intake of risk groups such as recreational fishermen (Table 3). Bilau et al. (2007) differentiated two groups of fishermen; group A who take every catch home and eat all of it (up to 86 g eel/day) and group B who take their catch home sporadically and only eat half of it (12 g eel/day). These groups are exposed to ΣPBDEs ranging between 94–68,000 ng/day and 13–9500 ng/day, for risk groups A and B, respectively and to ΣHBCDs ranging between 95–32,800 ng/day and 13–4600 ng/day, for risk groups A and B, respectively. Table 3 shows dietary intakes of normal consumer and risk groups.

Reference dose (RfD) values have been calculated based on animal *in vivo* studies (Table 4). These are an estimate of daily exposures of the human population (including sensitive subgroups) which are likely to be without an appreciable risk of deleterious effects during a lifetime. For an individual of 70 kg, a daily intake above 7000 ng BDE 47 and 14,000 ng HBCD are expected to cause health risks. As BDE 47 is the most abundant congener in eels, consumers of polluted eel from risk group A are being exposed well above these values.

4. Conclusions

Current PBDE and HBCD concentrations in Flemish eels vary widely according to the sampling area. Discarding the higher values, concentrations are in line with what has been observed in previous European studies. BDE 47 is the major congener and α-HBCD is the major isomer in all eel samples. Profiles in sediment differ from those in eels and no correlation between both matrixes was found. Although maximum concentrations of PBDEs and HBCDs have declined substantially during recent years, high concentrations were detected near industrialized areas. Intake of PBDEs and HBCDs, through consumption of contaminated eel, is below the RfD values for the average population (Table 4), although the exposure of risk groups significantly exceeds these levels. The current data show an ongoing exposure of eels to BFRs through indirect release from sediment and soils and therefore concerns are raised regarding the impact of BFRs on eels and on the human exposure close to industrialized hotspots. The current study advises ongoing monitoring of PBDEs and HBCDs in Flemish waters, particularly in the tideway of the river Scheldt.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.envint.2010.03.001.

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